Review

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A novel approach to the green synthesis of metallic nanoparticles: the use of agro-wastes, enzymes, and pigments

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Abstract: The green synthesis of nanoparticles has received great attention in recent times owing to its advantages such as cost effectiveness, simplicity, eco-friendliness, biocompatibility, and wide applications over the conventional chemical and physical methods. Various kinds of biomolecules from microorganisms and plants have been successfully utilized for the synthesis of metallic and nonmetallic nanoparticles, and these have been well documented. However, the recent increase in the fabrication of metallic nanoparticles using agro-wastes, enzymes and microbial and plant-derived pigments and their respective areas of applications have not been compiled as a review article. Therefore, the present efforts have been aimed at compilation of reports on the use of these novel bio-resources for the green synthesis of nanoparticles. To the best of our knowledge, this is the first review article on the green synthesis of metallic nanoparticles using diverse agro-wastes, enzymes, and pigments of biological origin. It is envisaged that the compendium will bring to the fore the emerging importance of these bio-resources for nanobiotechnological applications.

Keywords: agro-wastes; enzymes; green synthesis; nanoparticles; pigments.

1 Introduction

The green synthesis of nanoparticles is an emerging branch of nanotechnology in which environmentally benign materials in the form of whole cells, metabolites, or extracts from plants and microorganisms are used for the synthesis of metallic nanoparticles. It is advantageous over chemical and physical methods as it is safe, simple, cost-effective, relatively reproducible, and often results in more stable materials [1, 2]. The integration of the principles of green chemistry with nanotechnology has become a key area in nanoscience and has received great attention in recent years. Biological methods are used in the synthesis of metal and metal oxide nanoparticles of desirable size and morphology as they enhance the properties of nanoparticles in greener route. The method is devoid of the use of toxic chemicals that are found in the synthetic protocols which have adverse effects on the environment. Due to the rich biodiversity of plants and their potential secondary metabolites, plants and plant parts have been well exploited in recent times in the synthesis of a variety of nanoparticles [3]. Plant extracts contain abundant natural compounds such as alkaloids, flavonoids, saponins, steroids, tannins, and other nutritional compounds. These products are obtainable from various parts of plants such as leaves, stems, roots, shoots, flowers, barks, and seeds. They act as reducing and stabilizing agents for the bioreduction reaction in the synthesis of metallic nanoparticles. Plants have been used successfully in the synthesis of various greener nanoparticles such as cobalt, copper, silver, gold, palladium, platinum, zinc oxide, and magnetite [4].

Exploitation of food and commercial valued plant products for nanoparticles synthesis reduces the overall efficacy of the biosynthetic process because of competition for use as food materials or for other economic purposes. However, utilization of plentiful agro-waste resources is an eco-friendly method of synthesis and a sustainable way for effective utilization and management of plant wastes and biomass [5]. Nanoparticles have been successfully synthesized by a variety of agro-wastes such as *Cocos nucifera* coir, corn cob, fruit seeds and peels, wheat bran, rice bran, and palm oil mill effluent [6–10]. These agro-wastes have been found to be rich

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in biomolecules such as flavonoids, phenolics, and proteins that can serve as bioreductant agents in the green synthesis of diverse metallic nanoparticles. In our laboratory, we have extended the frontier of usage of agro-wastes in the synthesis of silver nanoparticles (AgNPs) using the extracts of kola seed shell [11], kola pod [12], and cocoa pod husk [13].

Enzyme-mediated synthesis of nanoparticles is one of the recent advancements in the field of nanotechnology. In most cases, active enzymes catalyze the formation of nanoparticles, whereas under some conditions, enzymes are denatured to release amino acids which act as reducing and stabilizing agents in the synthesis of nanoparticles. At times, the enzyme itself may act as a reducing and capping agent in the formation of nanoparticles. Pure α-amylase has been used in the synthesis of gold nanoparticles (AuNPs), in which the catalytic activity of the enzyme was still retained in the AuNP-α-amylase complex [14]. Other microbial enzymes that are relevant in nanoparticles synthesis are laccase, ligninase, cellulase, nitrate reductase, and sulfite reductase [15–17]. Recently, we reported the synthesis of AgNPs using crude keratinase [18] produced by a feather-degrading *Bacillus safensis* LAU 13 isolated from a feather dump site [19, 20], and extracellular laccase of *Lentinus edodes* [21]. Therefore, there is an increasing use of enzymes in the green route synthesis of nanoparticles.

Also, among the biomolecules that have been well exploited in green nanotechnology are pigments obtained from plants and microorganisms. Some possess biological properties which make them suitable for biomedical applications. For instance, the antimicrobial activity of actinorhodin pigment produced by *Streptomyces* sp. was improved when used in the formation of AgNPs [22]. Similarly, AgNPs have been synthesized from a pigment produced by *Streptomyces coelicolor* klmp33. The particles displayed remarkable antimicrobial activity against extended-spectrum beta-lactamase (ESBL) producing *E. coli* [23]. Other pigments include cochineal, flexirubin, fucoxanthin, melanin, phycocyanin, and C-phycoerythrin [24–29].

Metallic nanoparticles are widely recognized due to their wide range of applications such as catalysis, electronics, optics, and fabrication of nanodevices [30]. The advent of greener methods of synthesis has extended the areas of applications to pharmaceutical and biomedical fields because of their biocompatibility nature. This article, therefore, reviewed various greener methods that involved the use of agro-wastes, pigments, and enzymes of plants and microbial origins in the synthesis of metallic nanoparticles. Until now, there is no review that details the use of these novel materials in the green synthesis of nanoparticles.

2 Synthesis of nanoparticles by agro-wastes

Various types of metallic nanoparticles have been successfully synthesized from agro-industrial wastes. In most cases, extracts from these wastes were used as reducing and stabilizing agents for their syntheses (Table 1) with diverse activities ranging from antimicrobial, antioxidant, larvicidal, catalytic to cytotoxicity against cancer cells. These agro-wastes are abundantly produced during the processing of agricultural wastes, and often discharged into the environment with the attendant pollution. Most often, they are of poor nutritional quality and may even contain anti-nutritional factors that limit their applications as animal feeds [48]. Several biotechnological processes have been developed towards utilization of agro-wastes to improve the nutritional qualities by solid-state fermentation [48], production of enzymes [49, 50], organic acids [51], and as renewable materials for the production of biogas [52]. A further attempt at expanding the utilization of agro-wastes as sources of biomolecules in green nanotechnology has gained tremendous attention, whereby several agro-wastes (Figure 1) have been documented for their relevance in nanobiotechnology. Generally, the extracts containing active biomolecules that catalyze the formation of nanoparticles can be obtained through simple procedure of hot water extraction of dried and ground agro-waste materials. A typical example shown in Figure 2 is the processing of kola nut pod for the biosynthesis of AgNPs.

2.1 Silver nanoparticles

Pomegranate fruit peel extract was used to reduce silver and gold ions to form AgNPs and AuNPs, respectively [53]. The AgNPs which absorbed maximally at 427 nm were polydispersed and spherical in shape. The authors proposed that ellagic acid, a naturally occurring phenolic compound abundantly present in the fruit peel, was responsible for the formation of nanoparticles through its electron loss capacity. X-ray diffraction (XRD) study confirmed the particles to be face-centered cubic in symmetry with an average size of 5–10 nm. The same material was also used for the synthesis of spherical AgNPs

Table 1: Synthesis of nanoparticles by agro-wastes.

Extract	Reaction condition	Types of nanoparticles	Size (nm)	Shape	Applications	References
Pomegranate fruit peel	1 mM $AgNO_3$+5 ml of extract for 24 h	AgNPs	5–50	–	Antibacterial	[31]
Rambutan peel extract	1 ml extract+10 ml of 1 mM $AgNO_3$	AgNPs	132.6±42	Triangle, truncated triangle, and hexagonal	Free radical scavenger	[32]
Rambutan peel extract	$Zn(NO_3)_2 \cdot 6H_2O$+extract. Reaction at 80°C for 2 h	ZnO nanocrystal	–	–	Antibacterial	[33]
Rambutan peel extract	0.1 M $Ni(NO_3)_2 \cdot 6H_2O$+10 ml extract under magnetic stirring at 80°C for 2 h	NiO nanocrystal	50	–	Antibacterial	[34]
Annona squamosa peel extract	10 ml of extract+80 ml of 1 mM $AgNO_3$ at 25°C and 60°C, 4 h	AgNPs	35±5	Irregular spherical	–	[35]
Oak fruit hull extract	40 g/l extract+1 mM $AgNO_3$, pH 9 and temperature 45°C	AgNPs	40	Spherical	Cancer therapy	[36]
Cocos nucifera coir extract	80 ml of 1 mM $AgNO_3$+20 ml extract at room temp, 200 rpm, and 1 h	AgNPs	23±2	Spherical	Larvicidal	[8]
Punica granatum peel extract	100 ml extract+40 ml of 1 mM $H_2PtCl_6 \cdot 6H_2O$ at 90°C, 500 rpm for 30 min	Pt-NPs	16–23	Spherical	Catalyst	[37]
Wheat bran xylan	1 ml of 1 mM $AgNO_3$+alkaline xylan solution, at 100°C for 30 min	AgNPs	20–45	Spherical	Antioxidant and fibrinolytic activities	[10]
Citrus peel	5 ml extract+50 ml of 1 mM $AgNO_3$ at 30°C for 40 min	AgNPs	5–20	Spherical	Biomedical	[7]
Grape waste	1 mM catechin+1 mM $HAuCl_4$ for 1 min, 25°C	AuNPs	20–25	–	Medical	[38]
Lemon peel	3 ml extract+40 ml of 1 mM $AgNO_3$ at room temp for 5 h	AgNPs	17.3–61.2	Spherical	Antidermatophytic activity	[39]
Watermelon rind	20 ml of 1 mM $PdCl_2$+10 ml extract at 30°C, 150 rpm for 24 h	PdNPs	96	Spherical	Catalytic activity	[40]
Watermelon rinds	2.26 g of $FeCl_3 \cdot 6H_2O$ and 6.46 g of sodium acetate were dissolved in 30 ml extract, vigorous stirring at 80°C for 3 h	Fe_3O_4MNPs	2–20	Spherical	Catalyst	[41]
Groundnut peel	2 ml extract+98 ml of 1 mM $AgNO_3$ at 28°C for 60 min	AgNPs	20–50	Spherical	Larvicidal activity	[42]
Jatropha waste	25 ml of $HAuCl_4 \cdot 3H_2O$ solution (50 mg of $HAuCl_4 \cdot 3H_2O$ in 120 ml of double distilled water)+varied quantity of extract (7–20 ml) at room temp for 1 h	AuNPs	Approx. 14	Triangular, hexagonal, and spherical	–	[43]
Moringa oleifera flower	1 ml extract+49 ml of 1 mM $HAuCl_4$ solution at room temperature with stirring	AuNPs	28	Spherical	Antibacterial	[44]
Teak waste	100 ml of 1 mM $AgNO_3$+25 ml extract at 28°C±2°C with agitation	AgNPs	28	Spherical	Antibacterial	[5]
Cola nitida seed shell	40 ml of 1 mM $AgNO_3$+1 ml extract at 30°C±2°C	AgNPs	5–40	Spherical	Antibacterial	[11]
Cola nitida pod	40 ml of 1 mM $AgNO_3$+1 ml extract at 30°C±2°C	AgNPs	12–80	Spherical	Antibacterial, antifungal, additive in paint, and antioxidant	[12]

Table 1 (continued)

Extract	Reaction condition	Types of nanoparticles	Size (nm)	Shape	Applications	References
Cola nitida pod	8 ml of 1 mM $AgNO_3$+2 ml of 1 mM $HAuCl_4$+1 ml extract at 30°C±2°C	Ag-AuNPs	12–91	Rod, spherical, hexagonal, and triangular	Antifungal, dye degradation, larvicidal, anticoagulant, and thrombolytic	[45]
Cola nitida seed shell	8 ml of 1 mM $AgNO_3$+2 ml of 1 mM $HAuCl_4$+1 ml extract at 30°C±2°C	Ag-AuNPs	10–40	spherical	Antifungal, dye degradation, larvicidal, anticoagulant, and thrombolytic	[45]
Cocoa (*Theobroma cacao*) pod husk	40 ml of 1 mM $AgNO_3$+1 ml extract at 30°C±2°C	AgNPs	4–32	Spherical	Antibacterial, antifungal, synergistic, additive in paint, antioxidant, and larvicidal	[13]
Egg shell membrane (ESM)	2.4 mg of membrane+1 ml $HAuCl_4$ for 1.5 h	AuNPs	25±7	Spherical	Biosensing	[46]
Egg shell membrane	Dried ESM incubated with $HAuCl_4$ of varying concentrations of 0.1 mM–0.1 M	AuNPs	<20	Spherical, hexagonal, and triangular	Bioimaging and biolabeling	[47]

by Shanmugavadivu et al. [31]. Scanning electron microscopy (SEM) analysis revealed 5–50 nm as the average particle size, which absorbed maximally at 371 nm. The Fourier transform infrared spectroscopy (FTIR) showed involvements of primary and secondary amines, and other aromatic groups as facilitators of AgNPs synthesis. The particles showed tremendous antibacterial activity of 26 mm at a concentration of 2 mg/l against *Staphylococcus aureus* ATCC 25923. Similarly, Edison and Sethuraman [54] have used *Punica granatum* peel extract to synthesize AgNPs. The formation was confirmed by the appearance of brownish yellow color with the surface plasmon resonance (SPR) peak obtained at 432 nm. The particle size was approximately 30 nm with distorted spherical shape, and high negative zeta potential values revealed their high stability. The synthesized AgNPs effectively catalyzed the instantaneous reduction of anthropogenic pollutant, 4-nitrophenol (4-NP) by solid sodium borohydride. Kumar et al. [32] reported the synthesis of AgNPs using the peel extract of *Nephelium lappaceum* L. (Rambutan). The particles showed two peaks on the UV-vis spectra at 370 and 495 nm, respectively, and transmission electron microscopy (TEM) revealed the formation of triangle, truncated triangle, and hexagonal shapes with an average size of 132.6±42 nm. The particles were crystalline in nature with face-centered cubic symmetry according to selected area electron diffraction (SAED) and XRD analyses. The free radical scavenging activity of 80% displayed by the particles against 2, 2-diphenyl-1-picrylhydrazyl (DPPH) was remarkable, indicating their relevance in biomedicine.

A biosynthetic approach using oak fruit hull extract for AgNPs formation has also been developed [36]. The determined optimum reaction condition was as follows: silver nitrate concentration, 1 mM; extract concentration, 40 g/l (4% w/v); pH 9; and temperature, 45°C. Both TEM and dynamic light scattering (DLS) showed that the synthesized particles were spherical in shape with an average size of 40 nm, while the zeta potential analysis indicated a long-term stability of the particles. The particles displayed mild cytotoxic activity against human breast cancer cell (MCF-7) with IC_{50} of 50 and 0.04 µg/ml for isolated AgNPs and dispersed AgNPs in the extract, respectively. Velmurugan et al. [55] used defatted cashew nut shell (CNS) starch to reduce silver ion for the formation of AgNPs. The synthesized particles were compared with the commercially available AgNPs; it was observed that the duo was structurally identical according to SEM, energy dispersive X-ray spectroscopy (EDS), and FTIR analyses. Silver was found predominant; they both have parallel functional groups with sizes ranging from 10 to 50 nm. Authors, therefore, concluded that the use of cost effective, renewable, and

Figure 1: Some agro-wastes used for the biogenic synthesis of nanoparticles.

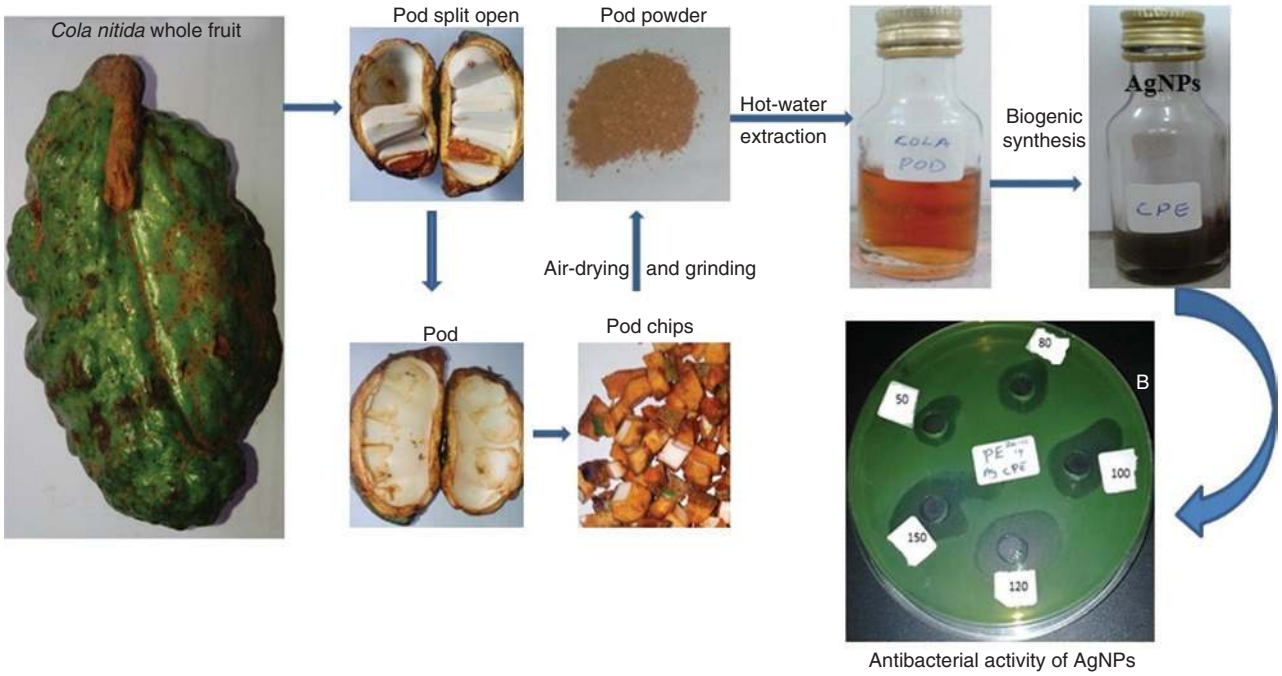

Figure 2: Schematic view of processing of kola nut pod for the biosynthesis of AgNPs with profound antibacterial activity.

environmentally friendly materials is a good alternative to laborious, toxic, and expensive physical and chemical methods of nanoparticles synthesis. Similarly, the use of CNS liquid for the synthesis of gold nanoparticles and AgNPs has been reported [56]. The synthesized silver and gold nanoparticles showed their maximum peak on

UV-vis absorbance spectrum at 440 and 546 nm, respectively. The TEM results revealed the particle sizes in the range of 5–20 nm with variations in shapes such as round, triangular, spherical, and irregular. Particles were crystalline according to XRD. The gold nanoparticles and AgNPs demonstrated remarkable antibacterial activity against fish pathogens.

The AgNPs were formed when Roopan et al. [8] made silver nitrate to react with aqueous extract of *Cocos nucifera* coir at 60°C. The synthesized particles showed maximum absorbance peak on UV-vis spectrum at 433 nm and TEM confirmed the particle size as 23±2 nm. The XRD spectrum showed the characteristic Bragg peaks of 111, 200, 220, and 311 facets of the face-centered cubic and crystalline AgNPs. The particles displayed larvicidal activity against *Anopheles stephensi* and *C. quinquefasciatus* with LC_{50} of 87.24 and 49.89 mg/l, respectively. When mango peel extract was investigated for nanoparticles synthesis by Yang and Li [57], the study led to the formation of crystalline, face-centered cubic AgNPs with size ranging from 7 to 27 nm as confirmed by XRD and TEM. The nonwoven fabrics impregnated with the particles displayed excellent antibacterial activity. Furthermore, the synthesis of irregular spherical shaped AgNPs with an average size of 35±5 nm from aqueous peel extract of *Annona squamosa* and silver nitrate have been reported [35]. Particles which absorbed maximally at 420 nm were formed in 4 h of reaction at 25°C and 60°C, respectively. From the extensive analysis of the extract using gas chromatography-mass spectrometry (GC-MS) and nuclear magnetic resonance spectroscopy (^{1}H NMR), authors concluded that water-soluble ketone and hydroxyl containing compounds were responsible for the catalytic reduction of silver ion to AgNPs.

Huang et al. [58] investigated the biosynthesis of AgNPs by *Cacumen platycladi* extract. The reaction involved the intermittent addition of silver nitrate solution to a constant amount of aqueous extract of *Cacumen platycladi*. It was observed that increasing the initial concentration of silver nitrate at 30°C or 60°C increased the mean size and widened the size distribution of the AgNPs as well as broadened the SPR absorption. The reducing sugars and flavonoids present in the extract were mainly responsible for the bioreduction of silver ions and this could be promoted at higher temperature such as 90°C as it led to the formation of AgNPs (18.4±4.6 nm) with a narrow size distribution through homogeneous nucleation. The biogenic AgNPs exhibited excellent antibacterial activity with minimum inhibitory concentration (MIC) of 1.4 and 5.4 ppm against *E. coli* and *S. aureus*, respectively. Furthermore, AgNPs have been synthesized using xylan obtained from wheat bran [10]. The xylan acted as a reducing and stabilizing agent in the reaction. The particles were polydispersed with size ranging from 20 to 45 nm and absorbed maximally at 405 nm. It displayed excellent free radical scavenging and fibrinolytic activities. The biosynthesized particles also demonstrated potential application in biomedicine as it remarkably dissolved preformed blood clots.

Kahrilas et al. [59] investigated the synthesis of AgNPs by aqueous extract of *Citrus* peels such as orange, grapefruits, tangelo, lemon, and lime. The synthesis of AgNPs was successful with orange peel extract within 15 min inside microwave at 90°C and 15 psi pressure showing maxima absorbance within 402–428 nm. The TEM analysis confirmed the particle size as 7.36±8.06 nm, and GC-MS indicated that aldehydes present in the extract were mainly responsible for the reduction and capping of synthesized AgNPs. The aqueous silver ions treated with the peel extract of Satsuma mandarin (*Citrus unshiu*) were reduced to mainly spherical AgNPs in the size range of 5–20 nm with a maximum absorbance at 440 nm [7]. Biogenic AgNPs were synthesized [60] on reacting fresh suspension of orange peel extract with aqueous silver ions at room temperature. The formation of AgNPs which was reportedly facilitated by flavonoids in the extract was confirmed by UV-vis spectroscopy which showed the maximum absorbance at 466 nm and Zitasizer which measured the particle size to be 91 nm. The synthesized particles displayed significant antibacterial activities on some Gram negative bacterial strains. Recently, Dauthal and Mukhopadhyay [61] reported the synthesis of AuNPs and AgNPs using *Citrus aurantifolia* peel extract. The particles were both spherical in shape with size ranging from 6 to 46 nm and 10 to 32 nm, respectively. They had face-centered cubic structure with high stability as obtained from XRD and zeta potential studies. The FTIR analysis revealed that citric and ascorbic acids in the peel extract were responsible for the reduction and stabilization of the nanoparticles. The biogenic nanoparticles demonstrated excellent catalytic activity in the reduction of anthropogenic pollutant, 4-nitroaniline in the presence of $NaBH_4$.

Nisha et al. [39] synthesized AgNPs by reacting extract of lemon peels with 1 mM of silver nitrate solution. The formation of AgNPs was confirmed by UV-visible spectrophotometer, field emission scanning electron microscope (FESEM), and energy dispersive X-ray spectroscopy (EDAX) analyses. The biosynthesized particles exhibited good antidermatophytic activity against multi-drug resistant *Candida albicans* and *Trichophyton mentagrophytes* to the tune of 11–12 mm. Bankar et al. [62] reported novel banana peel mediated synthesis of AgNPs with silver

nitrate. The extract obtained from crushed, boiled, acetone-precipitated banana peel extract (BPE) was used to reduce silver nitrate to form AgNPs. Reaction conditions such as pH, temperature, BPE contents, and silver nitrate concentration were varied to favor the particles formation. The AgNPs formation was confirmed by color change, UV-vis spectroscopy, XRD, SEM, and FTIR analyses. These particles possessed appreciable antimicrobial activity. Similarly, Ibrahim [63] reported the use of banana peel extract to synthesize spherical and monodispersed AgNPs which had maximum absorbance at 433 nm. The particles with an average size of 23.7 nm were formed due to the activities of pectin, cellulose, hemicelluloses, and proteins present in the extract, as evidenced from FTIR data. The AgNPs showed growth inhibitions of 12–20 mm against strains of *Bacillus subtilis*, *Staphylococcus aureus*, *Escherichia coli*, and *Pseudomonas aeruginosa*. It also enhanced the activities of an antibiotic, levofloxacin in a synergistic manner producing 1.16–1.32 fold improvement in antibacterial activities against the tested bacteria.

Velu et al. [42] synthesized AgNPs by reacting silver nitrate solution with groundnut (*Arachis hypogaea*) peel aqueous extracts at 28°C for 1 h. The biosynthesized particles have size ranging from 20 to 50 nm; they are crystalline with face-centered cubic structure. The FTIR data showed that polyphenolics, carboxyl groups, amino groups, and amino acid residues present in the extract were responsible for the formation of AgNPs. The particles displayed good larvicidal activity against the fourth instar larvae of dengue (*Aedes aegypti*) and malaria (*Anopheles stephensi*) vectors with LC_{50} of 1.85 and 3.13 ppm, respectively, in a 24 h study. Also, the synthesis of AgNPs by aqueous extract of teak (*Tectona grandis*) leaves as reducing and stabilizing agents at 28°C±2°C with agitation was reported by Devadiga et al. [5]. The characterization of the biosynthesized particles revealed that they were spherical with an average size of 28 nm and biomolecules present in the extract such as polyphenols, antioxidants, and flavonoids were responsible for the reduction and stabilization of the particles. The synthesized AgNPs demonstrated remarkable antibacterial activity against strains of *S. aureus* and *E. coli* with an MIC of 25.6 μg/ml.

Kumar et al. [64] have reported the synthesis of AgNPs using the extract obtained from Sacha inchi (*Plukenetia volubilis*) shell. The mixture of silver nitrate and the extract was in the ratio 10:1 and the reaction was allowed under indirect sunlight at pH 12 and 23°C. The synthesized AgNPs were mainly spherical with an average size of 7.2 nm, and possibly facilitated by the polysaccharides in the extract. The particles under sunlight catalyzed the remediation of methyl orange contaminated solution to the tune of about 60% degradation at pH 2, contact time of 5 h, and AgNPs concentration of 64 mg/l. Vilchis-Nestor et al. [65] reported a one-step green methodology for the synthesis of AgNPs using aqueous extract of *Camellia sinensis* (green tea) supported by a carbonaceous material (Ag-CM) originated from the pyrolysis of sewage sludge. The synthesized Ag-CM demonstrated very good catalytic activity in the degradation of methylene blue dye in aqueous solution without the effect of sunlight or UV radiation. The Ag-CM removed about 91% of 30 mg/l methylene blue in 9 h, whereas the carbonaceous material alone could only remove 60% of the dye in 30 h. Furthermore, the rapid synthesis of purple-brown colloidal AgNPs by latex extract of *Thevetia peruviana* has been investigated [66]. The particles were characterized and confirmed by standard characterization methods. The particles have characteristic SPR peak at 570 nm with spherical morphology and size distribution between 10 and 30 nm. Based on FTIR data, the study concluded that heterocyclic compounds and proteins present in the extract acted as capping ligands of the biosynthesized AgNPs.

In our laboratory, we have pioneered studies into the utilization of agro-wastes arising from the processing of certain tropical economic trees. The use of aqueous extract of seed shell of *Cola nitida* led to the formation of spherical AgNPs of 5–40 nm size [11]. The AgNPs which absorbed maximally at 454.5 nm were formed due to the catalytic roles of proteins and alkaloids in the extract. The MIC of 50 μg/ml was obtained against multi-drug resistant isolates of *Klebsiella granulomatis, E. coli*, and *P. aeruginosa*. In a related study, the aqueous pod extract of *C. nitida* was used to synthesize spherical AgNPs from $AgNO_3$ [12]. The AgNPs which absorbed maximally at 431.5 nm ranged from 12 to 80 nm in size. The FTIR data established the roles of proteins and alkaloids in the green synthesis of AgNPs. At concentrations of 50–150 μg/ml, the extract inhibited growth of *Klebsiella granulomatis, E. coli*, and *P. aeruginosa* to the tune of 12–30 mm. At 5 μg/ml, complete inhibitions of growth of *S. aureus, E. coli, P. aeruginosa, Aspergillus niger, A. flavus*, and *A. fumigatus* were achieved in AgNPs-paint admixture showing potential protective role in the suppression of microbial deterioration of emulsion paint. Furthermore, the AgNPs showed potent antioxidant activities with IC_{50} of 43.98 μg/ml against DPPH, and ferric ion reduction of 13.62%–49.96%. Most recently, cocoa pod husk extract was used to synthesize spherical AgNPs, which absorbed maximally at 428.5 nm [13]. The FTIR data showed that phenolics and proteins were responsible for the formation of AgNPs with sizes in the range of 4–32 nm. The AgNPs inhibited the growth of *E. coli* and *K. pneumoniae* with zones of 10–44 mm, while improved antibacterial activities

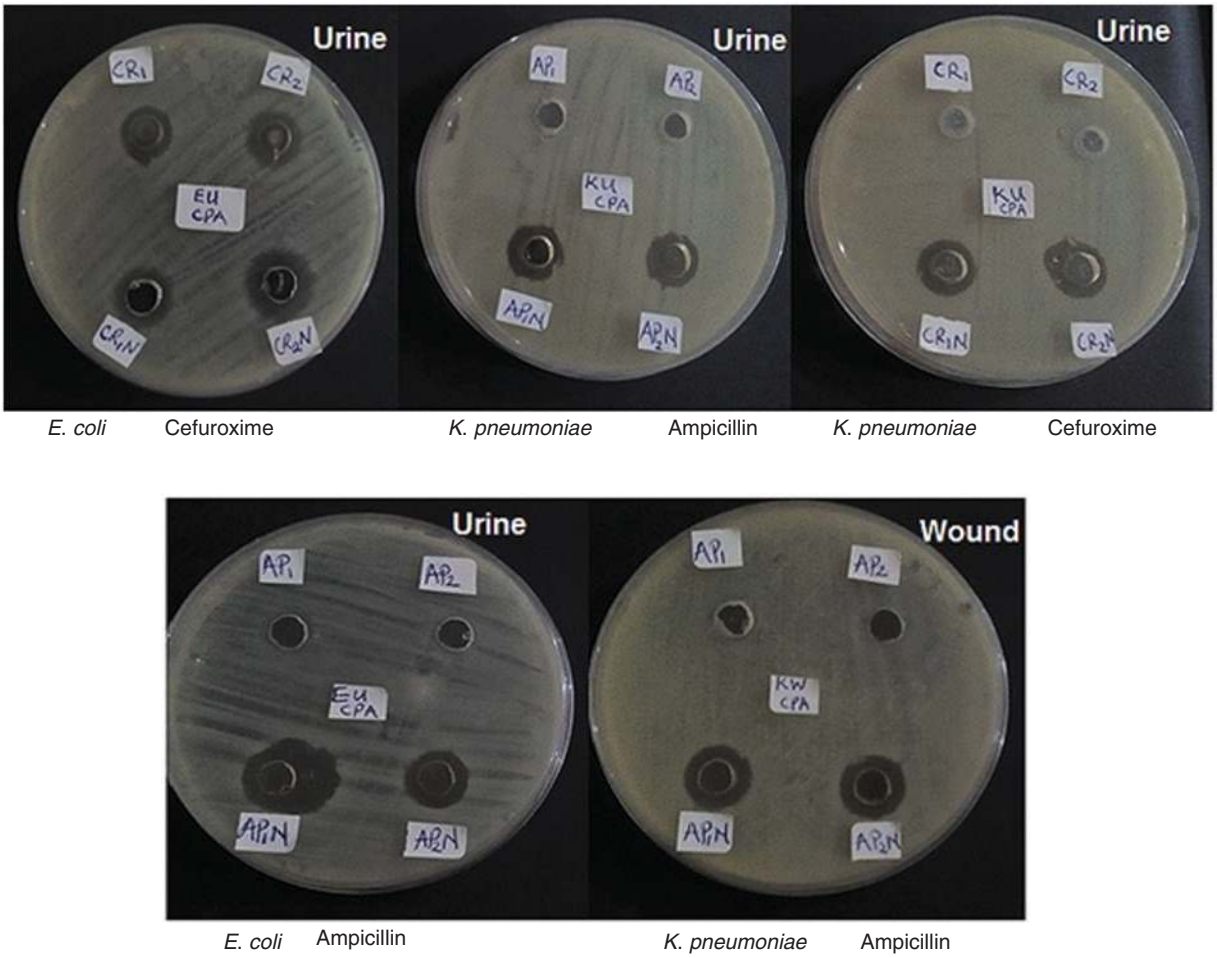

Figure 3: Synergistic activities of synthesized CPHE-AgNPs with ampicillin and cefuroxime on some clinical bacterial isolates.

of 42.9%–100% were achieved when the particles were used in synergistic studies in combination with cefuroxime and ampicillin (Figure 3). The particles also showed good DPPH scavenging (IC_{50} of 49.70 μg/ml), ferric ion reducing (14.44%–83.94%) and *Anopheles* mosquito larvicidal (LC_{50} of 43.52 μg/ml) activities. Also, it completely inhibited the growth of *E. coli*, *K. pneumoniae*, *Streptococcus pyogenes*, *S. aureus*, *P. aeruginosa*, *Aspergillus flavus*, *A. fumigatus*, and *A. niger* as additives in emulsion paint (Figure 4). The TEM images of some of the AgNPs biosynthesized in our laboratory as well as their SAED are as shown in Figure 5. Some of the materials can also be used to produce Ag-Au alloy nanoparticles (Figure 6), with single peak of SPR that indicates the formation of metallic alloys.

The novel use of animal wastes, particularly hen's egg shell and membrane have been used for the green synthesis of AgNPs. Apalangya et al. [67] reported the mechanochemical synthesis of AgNPs using the boiled egg shell as source of calcium carbonate to reduce silver ions to metallic particles. The spherical particles of 5–20 nm dimensions which absorbed maximally at 461 nm existed as hybrid composite with the calcite from the egg shell. The nanocomposite exhibited good antibacterial activity against *E. coli*. Similarly, Liang et al. [68] also used egg membrane to synthesize AgNPs through the involvement of functional groups present in the membrane. The nanocomposite AgNPs/ESM showed the presence of uniform distribution of small-sized AgNPs, which catalytically reduced 4NP to 4-aminophenol in the presence of borohydride. The study established the relevance of the natural membrane for the fabrication of hybrid nanocomposites for applications in different fields.

3 Gold nanoparticles

Yang et al. [69] used mango peel extract for the synthesis of AuNPs with size ranging from 6.03±2.77 to 18.01±3.67 nm.

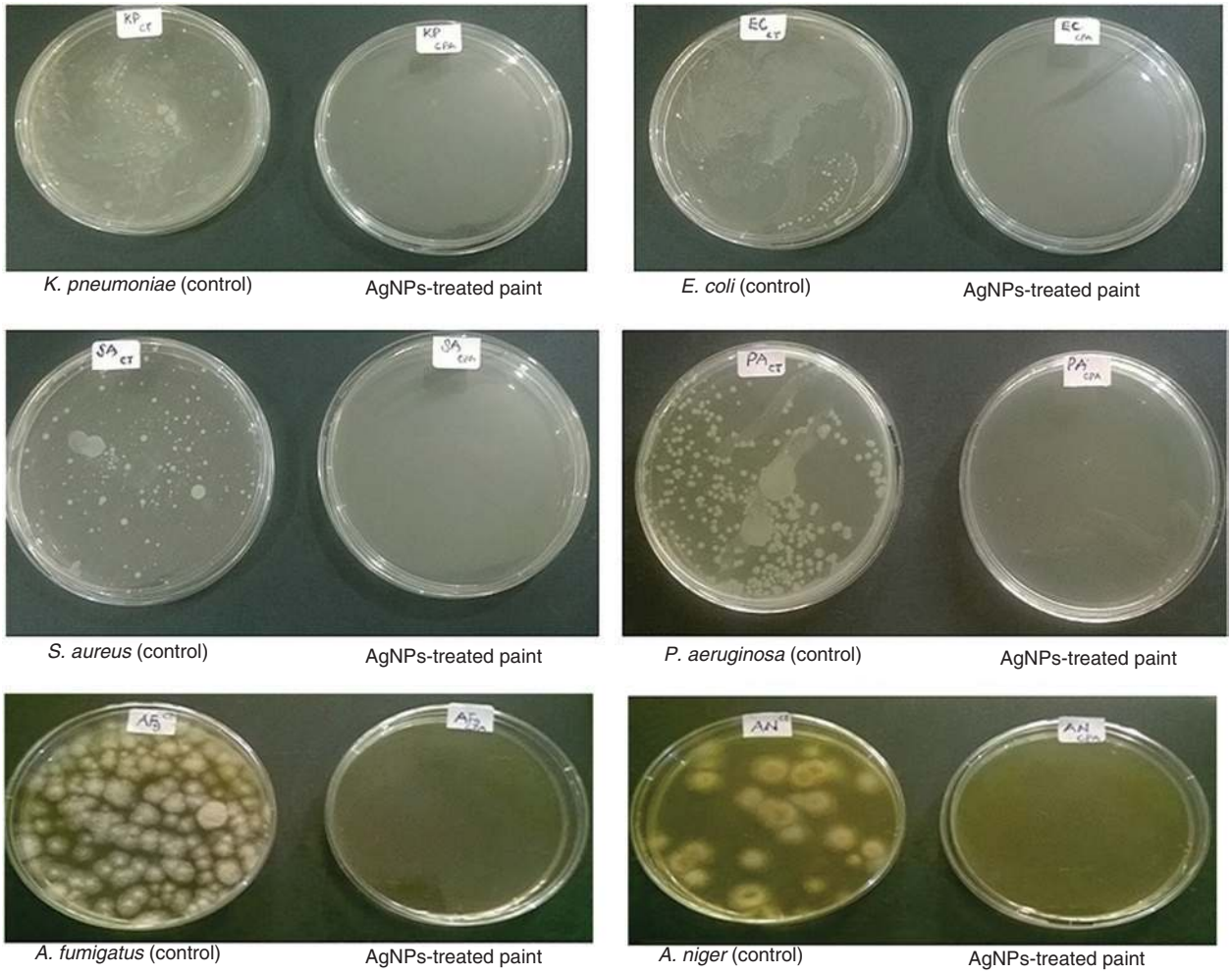

Figure 4: Antimicrobial activities of biosynthesized AgNPs using the cocoa pod husk extract when incorporated as an additive in emulsion paint.

The particles showed biocompatibility with African green monkey kidney normal cells (CV-1) and normal human fetal lung fibroblast cells (wI-38) at a high concentration of 160 µg/ml. Synthesis of AuNPs using rice bran extract was reported by Malhotra et al. [9]. The characterization of rice bran extract by high performance liquid chromatography and liquid chromatography-mass spectrometry revealed that ferulic acid in the extract was responsible for the reduction of Au^{3+} to Au^{0}. Grape wastes obtained after processing have been successfully used to synthesize 20–25 nm sized AuNPs in a single-step method at room temperature. The stable particles with maximal absorbance at 536–538 nm were formed within 5 min and characterized by UV-vis spectroscopy, high-resolution transmission electron microscope (HR-TEM), and EDX [38]. The study concluded that polyphenolic compounds such as catechin, epicatechin, anthocyanidin, proantocyanidin, and condensed tannins abundantly present in the grape wastes could be responsible for the formation of AuNPs. Furthermore, Patra and Baek [70] used aqueous extract of watermelon rind for the synthesis of AuNPs, which were spherical in shape and 20–140 nm in size and absorbed maximally at 560 nm. The synthesized particles facilitated by the catalytic action of phenolic compounds, flavonoids, lycopene, and citrulline exhibited potential antibacterial activity against some food-borne pathogens; *Bacillus cereus* ATCC 13061, *E. coli* ATCC 43890, and *Salmonella typhimurium* ATCC 43174 in the range of 9.23–11.58 mm. The combination of the particles with low concentrations of rifampicin and knamycin (5 µg/ml) led to improvement in antibacterial activities through synergy between the AuNPs and antibiotics. The particles also demonstrated significant antioxidant and anti-proteasome inhibitory potential, showing potential as an anti-cancer agent.

Similarly, Kanchi et al. [43] in their study reported a single-step green synthesis of AuNPs from aqueous extract

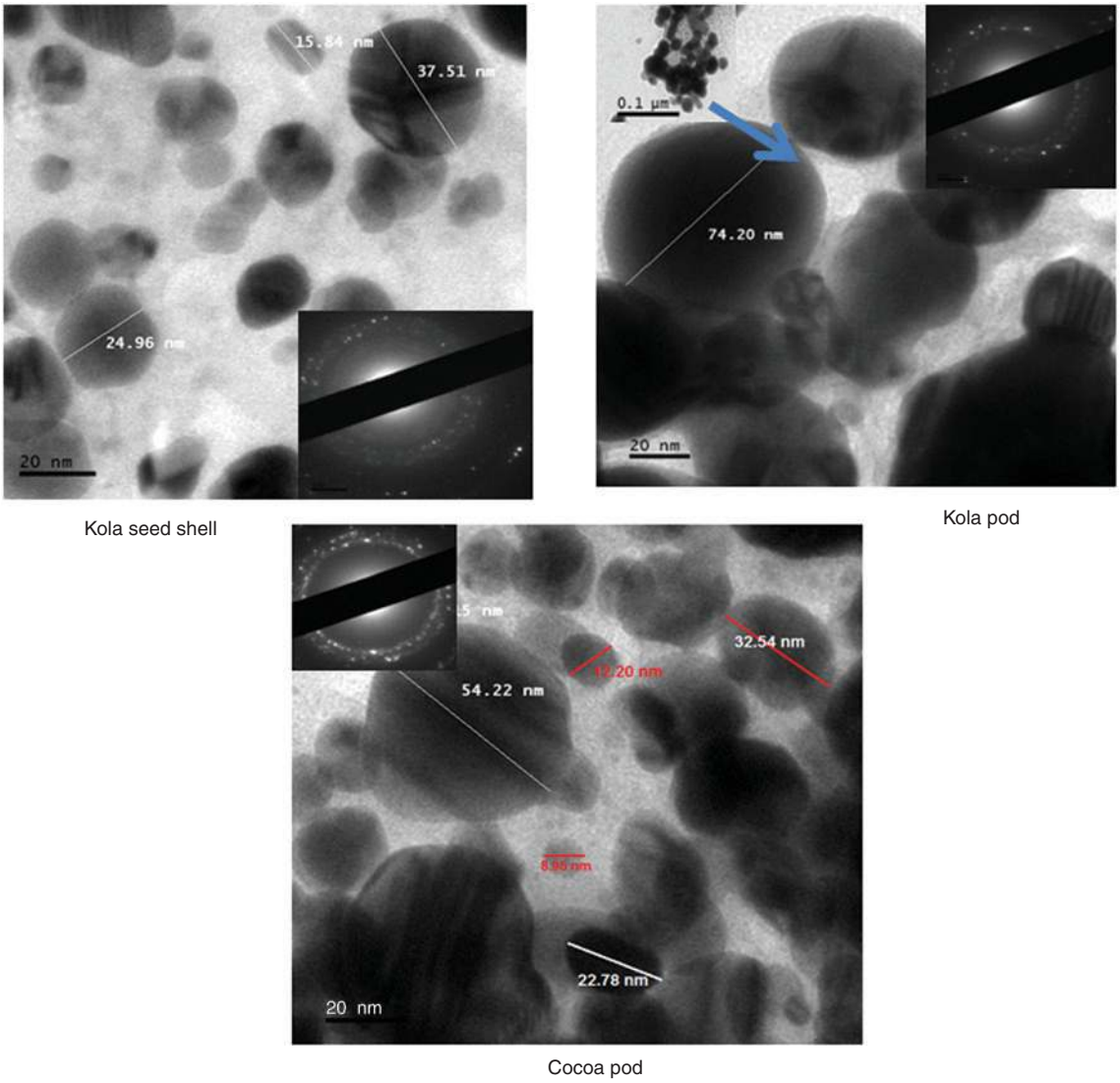

Figure 5: TEM images of biosynthesized AgNPs using some important agro-wastes (inset, SAED pattern).

of de-oiled *Jatropha* waste. Parameters such as temperature, pH, and concentration of the reacting molecules were optimized to favor the particles morphology. Hence, AuNPs (approximately 14 nm) of various shapes such as triangle, hexagonal, and spherical shape were obtained through the catalytic action of proteins present in the *Jatropha* waste. The peak SPR of the AuNPs was obtained at 520 nm. In the same way, Mohamed et al. [71] investigated the potential of seed shell and detoxified-defatted seed meal aqueous extracts of *Jatropha curcas* to synthesize AuNPs. AuNPs of uniform shape and size in the range of 5–20 nm were obtained in the optimized ratio of 1:1 (seed meal/shell:chloroauric acid) under constant shaking in water bath at 60°C. However, anisotropic particles of triangles, pentagons, rhombus, rod, pyramid, plates, needles, wires, diamonds, truncated flakes, spheres, and Au dots were obtained upon increase in the concentration of reducing agents, temperature, and pressure. Biosynthesized AuNPs were characterized by UV-vis spectroscopy, HRTEM, atomic force microscope (AFM), FTIR, and thermogravimetric analysis. The particles which absorbed maximally at 540 nm showed the involvement of protein molecules in the biosynthesis. The AuNPs displayed high level of biocompatibility (more than 90% cell viability of brain cancer glioma GI-1, and neuronal HCN-1A cell lines), efficient bio-imaging, and photoluminescent properties. Laser exposure of cancer cells treated with AuNPs led to the killing of cancer cells thereby establishing the cancer therapeutic potential of the AuNPs through photothermal ablation.

Similarly, Anand et al. [44] reported the synthesis of AuNPs using aqueous extract of *Moringa oleifera* flower

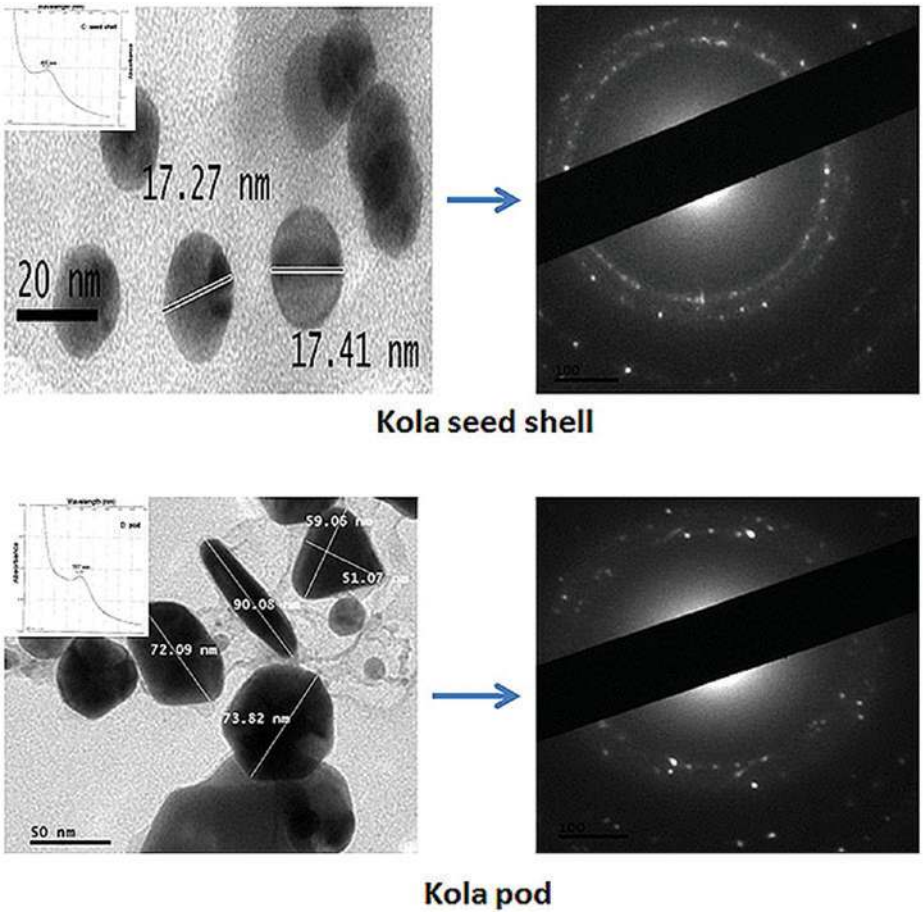

Figure 6: TEM images of biosynthesized Ag-AuNPs using some important agro-wastes (inset, UV-Vis absorption spectrum).

through the activities of proteins, carotenoids, phenolics, flavonoids, alkaloids, glycosides, and sterols present in the extract. The biosynthesized particles showed characteristic UV-vis absorption peak at 540 nm. The particles were reported to be well dispersed; triangular, hexagonal, and nearly spherical in shape with approximately 5 nm in size. The particles exhibited remarkable catalytic activity by rapidly reducing 4-NP and 4-nitroaniline. These biosynthesized particles also displayed anticancer activity. In addition, palm oil mill effluent had been successfully used as an agro-waste for the green synthesis of AuNPs, producing particles of average size of 18.75±5.95 nm. The particles were mainly spherical, with the presence of some triangular and hexagonal shapes [6].

Bankar et al. [72] reported novel banana peel mediated synthesis of AuNPs with chloroauric acid being the metallic precursor. The extract obtained from crushed, boiled, acetone-precipitated banana peel was used to reduce chloroauric acid to form AuNPs. Reaction conditions such as pH, temperature, BPE contents, and chloroauric acid concentration were varied to favor the formation of AuNPs. The synthesis was confirmed by color change, UV-vis spectroscopy, XRD, SEM, and FTIR analyses. The particles possessed appreciable antimicrobial activities against tested bacterial and fungal isolates.

Facile green synthesis of AuNPs using egg shell membrane has been reported by Zheng et al. [46]. AuNPs of core size of 25±7 nm was synthesized by immersing the membrane in chloroauric acid under ambient condition through the activities of aldehyde moieties present in the membrane. The synthesized AuNPs were formed on the immobilized membrane, and used to further immobilize glucose oxidase for the sensing of glucose. The study showed that egg shell membrane, which is an agro-waste, can be used for the green synthesis of AuNPs that has application in biosensing through complexation with glucose oxidase. In addition, Devi et al. [47] used egg shell membrane as a natural biotemplate to synthesize fluorescent AuNPs of varying shapes of sphere, triangle, hexagon, and truncated triangle. The synthesis of colloidal AuNPs was achieved *in situ*, resulting in the formation of particles of <20 nm. The study showed that aldehyde and

amino functional groups in the membrane were responsible for the synthesis of AuNPs with blue (437±5 nm) and red (630±5 nm) emissions that may be suitable for application as bioimaging and biolabeling agent.

4 Zinc, nickel, platinum, palladium, and magnetic iron oxide nanoparticles

Yuvakkumar et al. [34] synthesized biogenic zinc oxide nanocrystals from rambutan peels as follows: zinc ellagate complex was formed by reacting Zn $(NO_3)_2 \cdot 6H_2O$ with rambutan peel extract at 80°C for 2 h. The zinc ellagate complex was thereafter oven dried at 40°C for 8 h and then calcinated in a muffle furnace at 450°C to get zinc oxide nanocrystals. The synthesis of zinc oxide nanocrystals facilitated by polyphenols through the p-track conjugation effect was confirmed using standard characterization studies such as XRD, SEM-EDX, X-ray photoelectron spectroscopy (XPS), and FTIR. The cotton fabric coated with zinc oxide nanocrystals exhibited a remarkable antibacterial activity against *E. coli* (18.5 mm) and *S. aureus* (23 mm) owing to the increasing ZnO nanocrystals adsorption on the cotton surface. In a similar study Yuvakkumar et al. [33] also reported for the first time, the successful synthesis of nickel oxide (NiO) nanocrystals via nickel ellagate complex formation using rambutan peels. The polyphenols in the extract facilitated the formation of NiO nanocrystals from Ni $(NO_3)_2 \cdot 6H_2O$. The cotton fabric coated with the synthesized NiO crystals showed strong antibacterial activities of 25 and 35 mm against *E. coli* and *S. aureus*, respectively.

Annona squamosa aqueous peel extract has also been utilized for the synthesis of palladium nanoparticles [73]. In this study, 80 ml of 1 mM palladium acetate, Pd $(OAc)_2$ was reacted with 10 ml of aqueous extract at 60°C for 4 h. The synthesized particles were characterized by UV-vis spectroscopy, XRD, and TEM. Spherical-shaped palladium nanoparticles were confirmed with average size of 100 nm. Also, the aqueous extract prepared from watermelon rind has been used as capping and reducing agents for palladium nanoparticles [40], whereby the involvement of polyhydroxyl groups in the extract for the synthesis Pd NPs was established. The Pd NPs with an average size of 96.4 nm, and polydispersity index of 0.243, showed potential catalytic industrial applications through Suzuki coupling reaction of aryl halide with phenylboronic acid at room temperature.

The synthesis of Fe_3O_4 magnetic nanoparticles had been achieved using the watermelon rind extract [41] in a reaction mixture of $FeCl_3 \cdot 6H_2O$ and sodium acetate under continuous stirring at 80°C for 3 h. The spherical-shaped biogenic particles of 2–20 nm size with tremendous magnetic response behavior were characterized by UV-vis spectroscopy, XRD, FTIR, DLS, AFM, and TEM. The particles which were formed through the activities of polyphenols in the extract displayed remarkable catalytic activities in the organic synthesis of 2-oxo-1,2,3,4-tetrahydropyrimidine derivatives with very good yields of 94%. Similarly, Venkateswarlu et al. [74] reported the synthesis of Fe_3O_4 magnetic nanoparticles through plantain peel extract. The biogenic particles were characterized by standard analytical techniques. The particles were spherical in shape and well dispersed. The TEM revealed that their size was below 50 nm. The biosynthesized Fe_3O_4 magnetic nanoparticles displayed excellent magnetic property with saturation magnetization of 15.8 emu/g.

Furthermore, Dauthal and Mukhopadhyay [37] recently reported the synthesis of platinum nanoparticles using *Punica granatum* peel extract. The synthesized particles were crystalline and spherical with a size range of 16–23 nm. The negative zeta potential of the particles indicated high stability. The FTIR analysis revealed that the hydroxyl and carbonyl functional groups present in polyphenolic compounds and their quinones of the peel extract were responsible for the capping and stabilization of the synthesized particles. The particles displayed good catalytic activity by reducing anthropogenic pollutant, 3-nitrophenol by $NaBH_4$. The extract of *Annona squamosa* was also successfully used for the formation of polydispersed; spherical shaped and 23±2 nm sized TiO_2 NPs [75]. The presence of hydroxyl group containing compounds was stated to be responsible for the catalytic action of the rambutan peel extract in the formation of palladium and nickel metallic nanoparticles.

From the foregoing, it is evident that agro-wastes have been used on a wider scale for the synthesis of different nanoparticles, although most prominently Ag and AuNPs due to their richness in diverse biomolecules that can serve as reducing and capping molecules. The abundance of the agro-wastes and diversity can be successfully exploited on a large scale for the biogenic synthesis of nanoparticles. The system is cost effective, and can create wealth and useful products through nanotechnology.

5 Synthesis of nanoparticles by enzymes

There exist different types of enzyme-mediated synthesis of nanoparticles (Table 2). Enzymes by their general

Table 2: Synthesis of nanoparticles by enzymes.

Enzyme	Reaction condition	Types of nanoparticles	Size (nm)	Shape	Applications	References
α-Amylase	40 ml α-amylase solution + 60 ml of 1 mM $AgNO_3$ at 25°C	AgNPs	22–44	Triangular and hexagonal	–	[76]
α-Amylase	2 ml of enzyme solution + $HAuCl_4/AgNO_3$ of mole ratio 1:1 at 70°C	Au/Ag NPs	63	Spherical	–	[77]
α-Amylase	α-Amylase incubated with $HAuCl_4$ solution at 37°C for 48 h	AuNPs	5–20	–	–	[14]
α-Amylase	25 ml of 0.25 M $TiO(OH)_2$ + 30 ml of α-amylase at 60°C for 10 min with agitation	TiO_2NPs	50	Hexagonal and spherical	Antibacterial	[78]
Bromelain	3 µl of 1 mM $HAuCl_4$ + 3 ml of bromelain at 40°C for 48 h	AuNPs	8.59–12.92	Spherical	–	[79]
Cellulase	100 µl of 5 mg/ml cellulose + 10% glycerol + 10 ml of 0.5 mM $AgNO_3$ for 24 h	AgNPs	5.04±3.50	Spherical	–	[17]
Nitrate reductase	Nitrate reductase + 10 ml of 1 mM $AgNO_3$ + 1 mM 8-hydroxyquinoline + 1 mM NADH at pH 7.2, 35°C and 150 rpm	AgNPs	10–20	Spherical	–	[80]
Keratinase	1 ml of keratinase (50 U/ml) + 50 ml of 1 mM $AgNO_3$ at 30°C±2°C for 2 h	AgNPs	5–30	Spherical	Antibacterial	[18]
Laccase	12 ml of laccase + 30 ml of 1 mM $AgNO_3$ at 28°C±2°C for 2 h	AgNPs	50–100	Spherical	Antibacterial	[21]
Laccase	200 µl of laccase + 1 mM $AgNO_3$ at 30°C–50°C	AgNPs	<100	Spherical	Antimicrobial	[81]
Laccase	3 ml of laccase (417 IU/mg) + 0.1 ml $HAuCl_4$ (10 mg/ml), reaction was stirred for 90 min	AuNPs	22–39	–	–	[82]

characteristics catalyze the synthesis but not get involved in the reactions, and sometimes may serve as reducing and stabilizing agents. The process may also be catalyzed by whole enzyme or amino acids released after denaturation of the enzyme by reaction conditions. In an excellent review, Durán et al. [83] showed the involvement of thiol groups and disulfide bridge moieties of enzymes as the reaction sites of nanoparticles formation. Similarly, the S-S and S-H moieties of denatured enzymes could transform metallic ions to nanoparticles. Therefore, nanoparticles can be formed by both enzymatic and nonenzymatic processes.

5.1 Silver nanoparticles

Talekar et al. [80] for the first time reported the synthesis of AgNPs using immobilized NADH-dependent nitrate reductase obtained from *Fusarium oxysporum* as cross-linked enzyme aggregates. The immobilized enzyme was repeatedly used for four cycles of AgNPs synthesis in batch mode with a catalytic yield of 90%. The synthesized AgNPs were 10–20 nm in size which absorbed maximally at 426 nm after 24 h of reaction. Earlier, α-NADPH-dependent nitrate reductase and phytochelatin agent were reported for the first time for the green synthesis of AgNPs of 10–25 nm size [84]. The Au-Ag bimetallic nanoparticles have also been synthesized by Raju et al. [85] using macerase enzyme as a reducing agent. The synthesis occurred at different temperatures, 80°C and 90°C, respectively, while the latter was found to be optimum. Characterization was done by UV-vis, TEM, and EDAX. The AgNPs were spherical in shape with 4–20 nm in size. The synthesized particles had inner gold and outer layer of silver bimetallic nanoparticles according to TEM analysis, and had maximum absorbance at 510 nm.

Also, the purified fibrinolytic enzyme obtained from *Bacillus cereus* NK1 formed AgNPs when incubated with 1 mM $AgNO_3$ for 24 h which absorbed maximally at 440 nm. The reaction was rapid upon the addition of NaOH solution and the reaction time for the synthesis of AgNPs was drastically reduced to 5 min yielding crystalline particles with spherical morphology. The synthesized AgNPs was 60 nm in size and the result of FTIR analysis revealed that protein molecules were responsible for the synthesis [86]. Mishra and Sardar [76] also used α-amylase to reduce silver ion for the formation of AgNPs at 25°C during 12 h of reaction. The particles showed maximum absorbance at the wavelength of 422 nm. The TEM analysis revealed that the particles were monodispersed (22–44 nm) with triangular and hexagonal shapes. The authors concluded that the technique used in the study could be explored for the

large-scale production of nanoparticles in an eco-friendly manner.

Recently, we reported the green synthesis of spherical and approximately ~8 nm size AgNPs under ambient condition (30°C±2°C) using keratinase produced by a novel strain of *B. safensis* LAU 13 isolated from feather wastes dump site [18]. With about 50 U/ml of the enzyme, AgNPs of 5–30 nm sizes, which absorbed maximally at 409 nm were formed. The FTIR data showed that proteins were responsible for the formation of AgNPs, which depicted good antibacterial activities against clinical isolates of *E. coli* to the tune of 8.6–12.5 mm. Earlier, Revathi et al. [87] reported the use of keratinase of a bacterium for the green synthesis of AgNPs with high absorbance within 400–450 nm. The particles reportedly inhibited the growth of *E. coli* and *S. aureus*.

Rai and Panda [17] have reported the cellulase-mediated synthesis of AgNPs both in buffer and methanol. In their study, 100 µl of 5 mg/ml cellulase obtained from *Trichoderma reesei* was dissolved in 20 mM phosphate buffer (pH 8.5) and incubated with 10 ml of 0.5 mM silver nitrate prepared with 10% glycerol for 24 h. The change in color from colorless to reddish brown suggested the formation of AgNPs. However, the synthesis of AgNPs in methanol was carried out by incubating 100 µl of 5 mg/ml cellulase prepared in 80% methanol with 10 ml of 0.5 mM of silver nitrate solution prepared in 95% methanol. The reaction was initiated by the addition of 40 µl of 0.01 M NaOH and the reaction mixture was left overnight. The change in color from colorless to golden brown indicated the formation of AgNPs. The synthesized AgNPs were further characterized by various spectroscopic and microscopic methods. The particles were narrow-sized (5.04±3.50 nm), and had absorption peak occurring at 420 nm. The FTIR data underscored the involvement of amino acids in the green synthesis of AgNPs.

Durán et al. [81] have reported the use of semi-purified laccase of *Trametes versicolor* for the green synthesis of AgNPs associated with AgCl nanoparticles typified by the presence of SPRs of 420–440, and 440–460 nm for AgNPs and AgCl nanoparticles, respectively. The FTIR showed that proteins were involved in the production of the spherical nanoparticles which were <100 nm in size, with proposition of cysteine-mediated (sulfhydryl group) synthesis in a nonenzymatic manner as a result of concomitant loss of laccase activity. The presence or formation of AgCl nanoparticles was ascribed to the semi-purification process of the laccase. We have also documented the first use of laccase of *Lentinus edodes* in the green synthesis of AgNPs, with the formation of walnut-shaped particles having a size range of 50–100 nm [21]. The particles which absorbed maximally at 430 nm, were formed through the activities of protein molecules as evidenced from FTIR data, and showed promising antibacterial activities of 11–20 mm against strains of *E. coli, P. aeruginosa*, and *K. pneumoniae*.

The use of lysozyme for the green synthesis of AgNPs has been reported by Eby et al. [88]. The hen egg-derived lysozyme catalyzed formation of spherical-shaped AgNPs from silver acetate dissolved in methanol without loss of hydrolase activity of the enzyme in the reaction mixture. The particles showed excellent activities against strains of *E. coli, Bacillus anthracis, S. aureus*, and *Candida albicans*. It was also reported to be active against drug and silver nitrate resistant *E. coli* and *Proteus mirabilis*. The biocompatibility of the AgNPs was established through its nontoxicity on epidermal keratinocytes at high concentrations that inhibited microbial growth. Kumar et al. [89] also studied the synthesis of Ag and AuNPs using hen egg lysozyme without any other reducing agents. The biocompatible particles were formed by the enzyme as evidenced by FTIR data which was denatured in the process. The particles showed potential antibacterial activities.

Moshfegh et al. [77] investigated the use of α-amylase as a reducing agent for the formation of metallic nanoparticles by considering five metal ions, including Cu^{2+}, Se^{4+}, Bi^{4+}, Au^{3+}, and Ag^{+} among which gold (AuNPs), silver (AgNPs), and gold/silver (Au/AgNPs) alloys nanoparticles were successfully synthesized. The synthesized AuNPs, AgNPs, and Au/AgNPs showed their maximum absorbance at wavelength of 530, 440, and 458 nm and their sizes were determined to be 89, 37, and 63 nm, respectively. Furthermore, Sharma et al. [90] reported the synthesis of several nanoparticles using Jack bean urease such as Ag, Au, Pt, and alloys of Ag-AuNP, Ag-PtNPs, and Au-PtNPs. The cysteine residue of urease was established to have catalyzed the biosyntheses with some partial loss of activity of the enzyme.

5.2 Gold nanoparticles

Kumar et al. [91] synthesized gold nanoparticles of size 7–20 nm using α-NADPH-dependent sulfite reductase and phytochelatin agent. Similarly, Gholami-Shabani et al. [92] successfully synthesized gold nanoparticles at 25°C for 60 s using cell-free purified α-NADPH-dependent sulfite reductase obtained from *E. coli*. The particles were spherical with an average size of 10 nm and a zeta potential of -30±0.2. The biosynthetic AuNPs showed strong antifungal activity against human fungal pathogens. In a related study, the synthesis of gold nanoparticles was

reported by Gupta et al. [93] using the combination of disulfide reductase and keratinase produced by a strain of *Bacillus subtilis* as reducing and stabilizing agents. The FTIR analysis revealed that protein molecules were responsible for the capping of the biogenic AuNPs. In a related development, Chinnadayyala et al. [94] developed a simple and single-step approach for the alcohol oxidase (AOx) protein-mediated synthesis of AuNPs in alkaline (pH 8.5) condition with simultaneous stabilization of the nanoparticles on the AOx protein surface under native environment. The synthesized AuNPs were conjugated with AOx and the conjugation was confirmed by advanced analytical and spectroscopic techniques. The AOx-AuNPs conjugate was used to fabricate amperometric alcohol biosensor that was successfully used for the detection of alcohol in beverage samples.

Venkatpurwar and Pokharkar [95] synthesized AuNPs at pH 7 and 25°C using the therapeutic enzyme, serratiopeptidase. The UV-vis spectroscopy, TEM, XRD, and FTIR confirmed the formation of AuNPs. The biosynthesized AuNPs serve as a carrier for the enzyme as it retains the enzyme activity as shown by *in vitro* casein agar plate method and *in vivo* anti-inflammatory activity performed in experimental animals. The particles remained stable after 6 months at 25°C as indicated by no shift in the surface plasmon band. Mishra and Sardar [96] reported the synthesis of AuNPs using α-amylase as reducing and stabilizing agents. The reaction was held at 25°C for 6 h and the synthesized particles were characterized by UV-vis spectroscopy, TEM, HR-TEM, XRD, and FTIR. The particles displayed good catalytic activity in the reduction of p-nitroaniline pollutant. Similarly, Rangnekar et al. [14] synthesized AuNPs by incubating α-amylase with $HAuCl_4$ solution at 37°C for 48 h. The synthesis was confirmed by UV-vis spectroscopy, TEM, XRD, and FTIR analyses. The enzymatic activity of α-amylase was retained on the biosynthesized AuNPs as shown by starch agar plate assay method. Also, the purified fibrinolytic enzyme obtained from *Bacillus cereus* NK1 formed AuNPs upon incubation with 1 mM $HAuCl_4$ for 60 h. The reaction was rapid upon the addition of NaOH solution and the reaction time was drastically reduced to 12 h. The particles were crystalline in nature with spherical morphology. The synthesized AuNPs was 20 nm in size, and the FTIR data revealed that protein molecules were responsible for the synthesis [86].

Purified laccase obtained from *Paraconiothyrium variabile* was utilized for the synthesis of AuNPs. The particles were synthesized in 20 min after the incubation of 0.6 mM $HAuCl_4$ with 73 U laccase at 70°C. The synthesized particles showed peak at 530 nm on UV-vis absorption spectra. Particles are well dispersed with size ranging from 71 to 266 nm according to TEM [82]. Sanghi et al. [16] reported the intracellular and extracellular synthesis of AuNPs by ligninase and laccase produced by *Phanerochaete chrysosporium*, respectively, within 90 min at 37°C. The biosynthesized particles have spherical morphology with size ranging from 10 to 100 nm as evident by atomic force microscopy (AFM). El-Batal et al. [97] have also reported the use of laccase obtained from *Pleurotus ostreatus* for the synthesis of AuNPs. The violet-colored colloidal solution absorbed maximally at 550 nm, and was monodispersed with a size range of 22–39 nm. The synthesis manifested through the activities of secondary amide structure. Recently, Khan et al. [79] investigated the synthesis of AuNPs by bromelain (cysteine protease). In their study, AuNPs of various shapes were produced by varying the concentration of bromelain and the incubation temperature. It was observed that the size of AuNPs increased with increase in both the concentration of bromelain and incubation temperature. The biosynthesized AuNPs were monodispersed with size ranging from 8.59 to 12.92 nm when 0.33 mg/ml bromelain was used at 40°C. These particles were stable for several months at ambient temperature.

5.3 Cadmium sulfide, selenium, titanium oxide, and platinum nanoparticles

Biosynthesis of CdS nanoparticles by *Fusarium oxysporum* was reported by Ahmad et al. [98]. The sulfate reductase enzyme produced by the fungus converted the sulfate ions to sulfide ions which subsequently reacted with Cd^{2+} ions and finally formed stable CdS nanoparticles. Furthermore, the purified α-amylase obtained from *Bacillus methylotrophicus* was reacted with Na_2SeO_3 for the formation of selenium nanoparticles (SeNPs) [99]. The formation of SeNPs occurred at 50°C and 70°C in various Na_2SeO_3 concentrations (1:2, 1:4, and 1:10) and was optimized by the addition of glucose. The green synthesis of semi-conductor ZnO nanocrystals has been documented by De La Rica and Matsui [100] through mild biological route.

Furthermore, Johnson et al. [78] used hydrolytic urease for the green synthesis of crystalline TiO_2 nanoparticles under environmentally benign conditions. The monodispersed particles were easily formed and had very high surface area that can readily find applications as photocatalysts and photovoltaics. Ahmad et al. [101] also reported the synthesis of monophasic crystalline TiO_2 nanoparticles using α-amylase as the main reducing and capping agent. The synthesis was confirmed by XRD, TEM, and FTIR. The particles demonstrated very potent

antimicrobial activity against Gram positive and Gram negative bacteria.

Additionally, Riddin et al. [102] reported the biosynthesis of platinum nanoparticles using two different hydrogenase enzymes produced by a mixed consortium of sulfate-reducing bacteria (SRB). In this experiment, a mixed consortium of SRB reduced Pt (IV) to Pt (0) through the intermediate cation Pt (II) in a two-step two-electron reduction mechanism involving two different hydrogenase enzymes. The platinum (IV) was first reduced to Pt (II) by an oxygen-sensitive novel cytoplasmic hydrogenase. The Pt (II) was thereafter reduced to Pt (0) nanoparticles by an oxygen-tolerated/protected periplasmic hydrogenase. TEM and EDX analyses were used to confirm the deposit of platinum nanoparticles into the periplasmic space.

6 Synthesis of nanoparticles by pigments

In recent years, several biological methods have been developed in nanotechnology that involved the use of various biological materials ranging from plants to microorganisms. Notable among them are bio-pigments (Table 3), although they have received very scanty attention compared to other biological materials.

6.1 Silver nanoparticles

Egorova and Revina [106] have utilized quercetin, a plant-derived pigment as a reducing and stabilizing agent in the synthesis of silver and copper nanoparticles of 2–3 nm size. Also, Manikprabhu and Lingappa [22, 23] synthesized AgNPs using actinorhodin produced by *Streptomyces coelicolor* as a reducing and capping agent. Some 15 ml of silver nitrate (10^{-3} M) was made to react with 1 ml of actinorhodin under direct sunlight. The reaction was hastened by photo-irradiation as the particles were formed within 20 min. The synthesized particles showed maximum absorbance between 400 and 450 nm. The XRD and TEM analyses confirmed its crystalline nature and particle size of 28–50 nm, respectively. The AgNPs both alone or in combination with antibiotics demonstrated excellent antibacterial activity against methicillin-resistant *Staphylococcus aureus* and ESBL producing *E. coli*. The reaction of 1 ml of actinorhodin with 20 ml of $AgNO_3$ (10^{-3} M) under microwave irradiation at a fixed frequency of 2.45 GHz yielded AgNPs within 90 s [107]. The particles were crystalline in nature with an average size of 50 nm according to XRD and TEM analyses.

Fierascu et al. [103] synthesized AgNPs using ethanolic extract of *Calendula officinalis*. The reaction mixture which consisted of 1 ml of extract and 5 ml of 1 mM $AgNO_3$ solution was kept overnight at room temperature. The reaction was visually monitored and it was observed that the color of $AgNO_3$ changed from yellow opaque to yellow transparent due to the excitation of SPR in the synthesized AgNPs. The particles were further characterized by UV-vis spectroscopy, FTIR, SEM, and energy dispersive X-ray fluorescence. These analytical studies also confirmed the presence of carotenoids and chlorophylls in the plant extract. The biosynthesized AgNPs displayed high antioxidant activity. Kumar et al. [28] reported the synthesis of AgNPs using natural dye of Cochineal (*Dactylopius coccus* Costa) at room temperature. The particles showed maximum absorbance peak at wavelength between 440 and 460 nm. They are spherical AgNPs with size ranging from 20 to 50 nm. The biosynthesized AgNPs demonstrated photocatalytic degradation of methylene blue dye under the influence of direct sunlight irradiation.

Also, polycrystalline AgNPs have been successfully synthesized using aqueous extract of diatoms *Amphora*-46 [26]. In their study, silver nitrate solution was added to aqueous extract of diatom cells to make a final concentration of 2×10^{-3} M silver nitrate. The reaction was catalyzed by light at temperature of about 35°C–40°C. The synthesized particles showed strong SPR found to be 415 nm by UV-vis spectroscopy. Further characterization by TEM, XRD, EDAX, and SAED confirmed polycrystalline spherical AgNPs of an average size of 20–25 nm and also identified the photosynthetic pigment fucoxanthin as the reducing and stabilizing agent. The biosynthesized AgNPs exhibited strong antibacterial activities against Gram positive and negative bacteria. Most recently, Apte et al. [25, 104] synthesized Au and AgNPs by melanin obtained from psychrotrophic yeast *Yarrowia lipolytica* NCNC 789. The effect of melanin on AgNPs synthesis was investigated by incubating 1 ml of 2.5 mM $AgNO_3$ solution with different concentrations of melanin (100, 150, 250, 500 µg). The reaction mixture was heated at 100°C for 10 min. AgNPs of remarkable properties were formed with 500 µg of melanin. The particles were monodispersed with an average size of about 15 nm. The biosynthesized Au and AgNPs were characterized by standard analytical techniques, and the duo displayed effective antibiofilm activities. Also, Patel et al. [27] reported the synthesis of AgNPs using a proteinaceous pigment C-phycocyanin obtained from cyanobacterial cells. The synthesis was carried out by reacting C-phycocyanin (5 mg/ml) in 10 ml of 1 mM aqueous $AgNO_3$ solution, pH 7 at 25°C under cool white fluorescent light (50 µmol photons m^{-2} s^{-1}) for 48 h. The

Table 3: Synthesis of nanoparticles by pigments.

Extract	Reaction condition	Types of nanoparticles	Size (nm)	Shape	Applications	References
Actinorhodin	15 ml of 1 mM $AgNO_3$ + 1 ml of actinorhodin under sunlight	AgNPs	28–50	Irregular	Antibacterial	[22]
Carotenoids	1 ml of pigment + 5 ml of 1 mM $AgNO_3$ at room temperature over night	AgNPs	65	–	Antioxidants	[103]
Flexirubin	10 ml of 1 mM $AgNO_3$ + 1 ml of flexirubin incubated at room temperature for 30 min	AgNPs	49	Spherical	Anticancer	[29]
Fucoxanthin	$AgNO_3$ solution + Fucoxanthin to give a final concentration 2 mM $AgNO_3$ under light	AgNPs	20–25	Spherical	Antibacterial	[26]
Melanin	1 ml of 2.5 mM $AgNO_3$ + 500 µg melanin heated at 100°C for 10 min	AgNPs	15	–	Antibiofilm	[104]
C-phycocyanin	C-phycocyanin (5 mg/ml) + 10 ml of 1 mM $AgNO_3$ incubated at 25°C, pH 7, under cool white fluorescent light (50 µmol photons m^{-2} s^{-1}) for 48 h	AgNPs	–	–	–	[27]
C-phycoerythrin	C-phycoerythrin + 0.25 mM $CdCl_2$ + 1 mM Na_2S	Cds NPs	5	Spherical	–	[24]
Blue pigment	1 ml of pigment + 20 ml of 1 mM $HAuCl_4$ under microwave irradiation for 10 s	Au nanorods	25–30	Irregular	–	[105]

synthesized particles were characterized by UV-vis spectroscopy, TEM, and EDS.

6.2 Gold, cadmium sulfide, titanium, and zinc oxide nanoparticles

Similarly, Manikprabhu and Lingappa [105] produced gold nanorods using blue pigment extracted from *Streptomyces coelicolor* klmp33 under a microwave-assisted condition. In the reaction, 1 ml of pigment was made to react with 20 ml of $HAuCl_4$ solution (10^{-3} mol l^{-1}) under microwave irradiation. At the initial 10 s of reaction, AuNPs of about 25–30 nm were formed. As the reaction progressed, after 30 s, gold nanorods of size 45 nm were synthesized, but at 90 and 120 s the size increased to 200 and 250 nm, respectively. These particles were characterized by visual inspection, UV-vis spectroscopy, TEM, FTIR, and XRD analyses. In another study, melanin obtained from a cold-adapted yeast (*Yarrowia lipolytica* NCYC 789) was used to synthesize gold nanostructures. The melanin-derived nanoparticles displayed antibacterial and anti-biofilm activities, which could be used to control biofilm formation [108].

Similarly, the pigment, C-phycoerythrin extracted from *Phormidium tenue* NTDM05 was used as a stabilizing and capping agent in the synthesis of CdS nanoparticles [24]. The particles were 5 nm in size according to TEM. De La Rica and Matsui [100] have also reported the use of urease to synthesize ZnO nanoparticles.

7 Conclusion

Biosynthesis of metallic nanoparticles has proven to be an effective alternative to the chemical and physical methods. The use of agro-wastes is of great advantage as it is one of the effective waste management processes and constitutes production of high-valued products from cheap materials. Microbial and plant-derived enzymes and pigments have also demonstrated good potential applications in the area of nanotechnology as they have been well utilized in the syntheses of nanoparticles of remarkable properties and applications. Richness of these materials in different biomolecules that can drive the process of synthesis of nanoparticles shall lead to economically viable means to produce nanoparticles on a larger scale through novel green approaches. This review has further underscored the emerging important roles that utilization of agro-wastes, enzymes, and biological pigments can play in the synthesis and applications of biocompatible nanoparticles in diverse areas of human endeavor.

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Bionotes

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